

DECLARATION

I, the undersigned, of 2-12, Nakazaki 2-chome, Kita-ku, Osaka, Japan, hereby certify that I am well acquainted with the English and Japanese languages, that I am an experienced translator for patent matter, and that the attached document is a true English translation of

Japanese Patent Application No. 2000-257259

that was filed in Japanese.

I declare that all statements made herein of my own knowledge are true, that all statements on information and belief are believed to be true, and that these statements were made with the knowledge that willful statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Signature:

A handwritten signature in cursive script, appearing to read 'Y. Iwasaka', written in dark ink.

Yoshiharu Iwasaka

Dated: April 23, 2003

[Name of Document] Specification

[Title of the Invention] INK FOR INK-JET RECORDING, AND INK
CARTRIDGE AND RECORDING APPARATUS INCLUDING THE SAME

[Claims]

5 [Claim 1] Ink for ink-jet recording, characterized by
containing an oil-soluble dye, a humectant, a penetrant,
water, and an amphiphilic star block polymer of which the
outer portion is hydrophilic.

10 [Claim 2] Ink for ink-jet recording, characterized by
containing an oil-soluble dye, a humectant, a penetrant,
water, and an amphiphilic heteroarm star polymer.

[Claim 3] The ink for ink-jet recording of Claim 1 or
2, characterized in that the viscosity is in the range of 1
to 10 mPa · s.

15 [Claim 4] A recording apparatus, characterized by
including the ink for ink-jet recording according to any one
of Claims 1 to 3.

20 [Claim 5] An ink cartridge, characterized by including
the ink for ink-jet recording according to any one of Claims
1 to 3.

[Detailed Description of the Invention]

[Technical Field to which the Invention Belongs]

25 The present invention relates to ink suitable for ink-
jet recording, and an ink cartridge and a recording apparatus
including such ink.

[Prior Art]

Conventionally, as ink used for ink-jet recording, the

ink containing a dye as a coloring material, a humectant, a penetrant, and water is well known. The humectant is contained for preventing drying of the ink on an ink head, while the penetrant is contained for improving the
5 penetration of the ink into recording paper.

As the dye, water-soluble dye is often used. To enhance water resistance on recording paper, however, oil-soluble dye is preferably used. As ink using an oil-soluble dye, known is ink essentially composed of an oil-soluble dye,
10 polyoxyethylene oxypropylenetriol and an aqueous acrylic resin solution or a water-soluble acrylic resin emulsion (see Japanese Laid-Open Patent Publication No. 10-140055). Also known is ink composed of a colored emulsion where a polymer obtained from a dye composition of a monomer composition
15 blended with an oil-soluble dye is dispersed in a water-type medium (see Japanese Laid-Open Patent Publication No. 2000-154341).

[Problems that the Invention is to solve]

By the way, ink used for ink-jet recording must be low
20 in viscosity to some extent. If the viscosity is too high, the ink fails to fly from a nozzle of an ink head in the form of an ink drop. The ink also must be sufficiently stable so as to be free from coagulating in an ink tank or clogging a nozzle and the like. However, none of the conventional ink
25 containing an oil-soluble dye was sufficient as the ink for ink-jet recording from the standpoints of low viscosity and stability.

For example, the ink disclosed in Japanese Laid-Open Patent Publication No. 10-140055 had viscosity of about 10000 mPa · s, which was too high for use for ink-jet recording. On the other hand, the ink disclosed in Japanese Laid-Open
5 Patent Publication No. 2000-154341 could have reduced viscosity, but was poor in stability. This ink therefore tended to coagulate during storage or clog an ink head.

As can be seen from the above, ink containing an oil-soluble dye and yet having low viscosity and high stability
10 has been desired as the ink suitable for ink-jet recording. The present invention has been made in view of said fact and its object is to provide ink for ink-jet recording that exhibits excellent water resistance on ordinary paper and provides recorded products with high printing quality and
15 high image quality, and a recording apparatus including such ink.

[Means for Solving the Problems]

In order to achieve the aforementioned object, the present invention provides ink containing an amphiphilic star
20 block polymer of which the outer portion is hydrophilic.

Specifically, the ink for ink-jet recording of a first invention contains an oil-soluble dye, a humectant, a penetrant, water, and an amphiphilic star block polymer of which the outer portion is hydrophilic.

25 The ink for ink-jet recording of a second invention contains an oil-soluble dye, a humectant, a penetrant, water, and an amphiphilic heteroarm star polymer.

In the above first and second inventions, oil-soluble dye molecules are captured by hydrophobic segments of an amphiphilic star polymer. The outer portion of the star polymer is hydrophilic and thus the star polymer itself
5 dissolves in water. The oil-soluble dye molecules that are captured in the inner portion of the star polymer also dissolve in water via the star polymer. As a result, the viscosity of the ink decreases and the stability thereof improves.

10 The ink for ink-jet recording of a third invention is the ink for ink-jet recording of the first or second invention, of which the viscosity is set in the range of 1 to 10 mPa · s.

The above third invention provides ink having
15 especially suitable viscosity for ink-jet recording.

The recording apparatus of a fourth invention includes ink for ink-jet recording of any one according to the first to third invention.

The above fourth invention allows a recording apparatus
20 to realize recording with high printing quality, high image quality, and excellent water resistance on ordinary paper.

The ink cartridge of a fifth invention includes ink for ink-jet recording of any one of the first to third inventions.

The above fifth invention allows an ink cartridge to
25 realize recording with high printing quality, high image quality, and excellent water resistance on ordinary paper.

[Embodiment of the Invention]

Hereinafter, an embodiment of the present invention will be described. FIG. 1 shows a schematic construction of an ink-jet recording apparatus in this embodiment. This recording apparatus jets ink from an ink-jet head 11 to allow
5 the ink to drop on recording paper 14 used as a recording medium so as to print characters or images on the recording paper 14. The ink-jet head 11, which is integrally equipped with an ink cartridge containing ink, is mounted with a carriage 12. The carriage 12 is provided with a carriage
10 motor not shown. With the carriage motor, the carriage 12 performs reciprocating motion in the main scanning direction X along a carriage axis 13 that extends in this direction. The carriage 12, the carriage axis 13, and the carriage motor constitute a relative movement means for moving the ink-jet
15 head 11 relatively with respect to the recording paper 14.

The recording paper 14 is interposed between two transport rollers 15, 15 that are rotated with a transport motor not shown, so that the recording paper 14 is transported with a transport motor and transport rollers 15,
20 15 in the sub-scanning direction Y orthogonal to the main scanning direction X.

The ink-jet head 11 stores, as ink for recording, ink containing an oil-soluble dye. In addition to the oil-soluble dye as a coloring material, the ink also contains a
25 humectant such as glycerin for suppressing drying of the ink on the head member, a penetrant such as diethylene glycol monobutyl ether for enhancing penetration of the ink into the

recording paper 14, and water. The ink further contains a star polymer.

As schematically shown in FIGS. 2 to 6, various types of star polymers exist. Among these, an amphiphilic star polymer of which the external portion is hydrophilic is particularly contained in the ink in this embodiment. In these figures, the reference numeral 16 denotes a hydrophilic segment, the reference numeral 17 denotes a hydrophobic segment, and the reference numeral 18 denotes a microgel.

Specifically, the ink in this embodiment contains an amphiphilic star block polymer as shown in FIG. 2 or an amphiphilic heteroarm star polymer as shown in FIG. 3. The reason why the types of star polymers used in this embodiment are limited to these two types is as follows.

As shown in FIG. 2, when ink contains an amphiphilic star block polymer where the hydrophilic segments 16 are located in the outer portion while the hydrophobic segments 17 are located in the inner portion, oil-soluble dye molecules 19 are captured by the hydrophobic segments 17.

That is, the oil-soluble dye molecules 19 are captured in the inner portion of the star polymer. On the other hand, since the outer portion of the star polymer is hydrophilic, the star polymer itself dissolves in water. As a result, the oil-soluble dye molecules 19 captured in the inner portion of the star polymer also dissolve in water via the star polymer. With the existence of such a star polymer in the ink, therefore, the viscosity of the ink is suppressed low

(preferably to 1 to 10 mPa · s). In addition, the stability of the ink is enhanced since the oil-soluble dye molecules 19 are less likely to coagulate with one another.

Likewise, as shown in FIG. 3, when ink contains an
5 amphiphilic heteroarm star polymer where both the hydrophilic segments 16 and the hydrophobic segments 17 extend from the microgel 18 and the hydrophilic segments 16 are longer than the hydrophobic segments 17, oil-soluble dye molecules 19 are captured by the hydrophobic segments 17 in high concentration.
10 Since the outer portion of this star polymer exhibits hydrophilicity, the star polymer itself dissolves in water. As a result, equally, the oil-soluble dye molecules 19 captured in the inner portion of the star polymer dissolve in water via the star polymer. Therefore, the viscosity of the
15 ink is suppressed low (for example, 1 to 10 mPa · s), and the stability of the ink improves.

On the contrary, the above effects of reduction in viscosity and improvement in stability are not obtained when an amphiphilic star block polymer as shown in FIG. 4 is used
20 where the hydrophilic segments 16 are located in the inner portion while the hydrophobic segments 17 are located in the outer portion. With the polymer having this construction, oil-soluble dye molecules 19 fail to be captured in the inner portion of the star polymer, and rather exist as weakly bound
25 coalescing masses in the outer portion of the star polymer. In addition, since the outer portion of the star polymer exhibits hydrophobicity, the star polymer itself does not

dissolve in water.

The above effects are not obtained either using a star polymer as shown in FIG. 5 where only the hydrophobic segments 17 extend from the microgel 18. In this case, although oil-soluble dye molecules 19 are captured by the hydrophobic segments 17, the star polymer having no hydrophilic segments fails to exhibit hydrophilicity and thus does not dissolve in water.

In using a star polymer as shown in FIG. 6 where only the hydrophilic segments 16 extend from the microgel 18, the polymer fails to capture oil-soluble dye molecules 19 in the inner portion. Therefore, in this case, also, the above effects are not obtained.

For the above reasons, an amphiphilic star polymer of which the outer portion is hydrophilic is selected in the ink in this embodiment.

Referring to FIG. 7, a star polymer as described above is prepared in the following manner. First, vinyl ether 1 is synthesized with HX/ZnX_2 ($X=Cl, I$) to obtain a living polymer 2 of polyvinyl ether with alkyl groups as side chains. The living polymer 2 is then reacted with divinyl ether 3 to give a star polymer 4.

Specifically, the amphiphilic star block polymer of which the outer portion is hydrophilic can be prepared by a synthesizing method shown in FIG. 8. In this synthesizing method, first, a living block polymer 5 of vinyl ether with ester side chains and alkylvinyl ether is reacted with

divinyl ether 3 to give a precursor star polymer 6. The side chains of this polymer are then hydrolyzed to obtain an amphiphilic star block polymer 7 having hydroxyl groups.

On the other hand, the amphiphilic heteroarm star
5 polymer can be prepared by a synthesizing method shown in FIG. 9. In this synthesizing method, first, a living block polymer of alkylvinyl ether is reacted with divinyl ether 3 to give a star polymer 8. The star polymer 8 is then reacted with the vinyl ether with ester side chains to give a
10 precursor star polymer 9. The side chains of this polymer are then hydrolyzed to obtain an amphiphilic heteroarm star polymer 10.

Examples of the oil-soluble dye contained in the ink include mono-azo dyes, dis-azo dyes, metal complex salt type
15 mono-azo dyes, anthraquinone dyes, phthalocyanine dyes, and triallylmethane dyes. Specifically, it is possible to use one type or two or more types in combination selected from C.I. Solvent Black #3, #5, #7, #22, #23, #27, #29, #34, #123, C.I. Solvent Blue #2, #11, #12, #25, #35, #36, #38, #55, #70, #73, C.I. Solvent Red #1, #3, #8, #23, #24, #25, #27, #30,
20 #49, #81, #82, #83, #84, #100, #109, #118, #121, #122, #132, #179, #218, C.I. Solvent Yellow #2, #6, #14, #15, #16, #19, #21, #33, #45, #56, #61, #77, #80, #82, #149, #151, C.I. Solvent Green #3, C.I. Solvent Orange #1, #2, #6, #14, #37, #40, #44, #45, C.I. Solvent Violet #8, #13, #14, #21, #27, and the like.

[Examples]

Hereinafter, specific examples carried out will be described.

First, 16 types of ink for ink-jet recording having the following compositions (shown in mass percentage) were prepared (Examples 1 to 16).

(Example 1)

C.I. Solvent Black #3	...	3%
Glycerin	...	10%
Diethylene glycol monobutyl ether	...	10%
10 Amphiphilic star block polymer (Formula 7)	...	2%
Pure water	...	75%

(Example 2)

C.I. Solvent Blue #2	...	3%
Glycerin	...	10%
15 Diethylene glycol monobutyl ether	...	10%
Amphiphilic star block polymer (Formula 7)	...	2%
Pure water	...	75%

(Example 3)

C.I. Solvent Red #1	...	3%
20 Glycerin	...	10%
Diethylene glycol monobutyl ether	...	10%
Amphiphilic star block polymer (Formula 7)	...	2%
Pure water	...	75%

(Example 4)

25 C.I. Solvent Yellow #2	...	3%
Glycerin	...	10%
Diethylene glycol monobutyl ether	...	10%

	Amphiphilic star block polymer (Formula 7)	... 2%
	Pure water	... 75%
	(Example 5)	
	C.I. Solvent Black #5	... 3%
5	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic heteroarm star polymer (Formula 10)	... 2%
	Pure water	... 75%
	(Example 6)	
10	C.I. Solvent Blue #11	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic heteroarm star polymer (Formula 10)	... 2%
	Pure water	... 75%
15	(Example 7)	
	C.I. Solvent Red #3	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic heteroarm star polymer (Formula 10)	... 2%
20	Pure water	... 75%
	(Example 8)	
	C.I. Solvent Yellow #6	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
25	Amphiphilic heteroarm star polymer (Formula 10)	... 2%
	Pure water	... 75%
	(Example 9)	

	C.I. Solvent Black #7	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic star block polymer	... 2%
5	(obtained by substituting an n-hexyl group for the isopropyl group of the star polymer in Formula 7)	
	Pure water	... 75%
	(Example 10)	
10	C.I. Solvent Blue #12	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic star block polymer	... 2%
	(obtained by substituting an n-hexyl group for the isopropyl group of the star polymer in Formula 7)	
15	Pure water	... 75%
	(Example 11)	
	C.I. Solvent Red #8	... 3%
20	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic star block polymer	... 2%
	(obtained by substituting an n-hexyl group for the isopropyl group of the star polymer in Formula 7)	
25	Pure water	... 75%
	(Example 12)	

	C.I. Solvent Yellow #14	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic star block polymer	... 2%
5	(obtained by substituting an n-hexyl group for the isopropyl group of the star polymer in Formula 7)	
	Pure water	... 75%
	(Example 13)	
10	C.I. Solvent Black #22	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic heteroarm star polymer	... 2%
	(obtained by substituting an n-hexyl group for the isopropyl group of the star polymer in Formula 10)	
15	Pure water	... 75%
	(Example 14)	
	C.I. Solvent Blue #25	... 3%
20	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic heteroarm star polymer	... 2%
	(obtained by substituting an n-hexyl group for the isopropyl group of the star polymer in Formula 10)	
25	Pure water	... 75%
	(Example 15)	

	C.I. Solvent Red #23	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic heteroarm star polymer	... 2%
5	(obtained by substituting an n-hexyl group for the isopropyl group of the star polymer in Formula 10)	
	Pure water	... 75%
	(Example 16)	
10	C.I. Solvent Yellow #15	... 3%
	Glycerin	... 10%
	Diethylene glycol monobutyl ether	... 10%
	Amphiphilic star block polymer	... 2%
	(obtained by substituting an n-hexyl group for the isopropyl group of the star polymer in Formula 10)	
15	Pure water	... 75%

Next, using the respective types of ink for ink-jet recording described above, recording was performed on ordinary paper (product name "Xerox 4024" available from Xerox Corp.) with a commercially available printer. These recorded paper sheets were immersed in pure water and then dried by leaving them at room temperature. The state of the ink on each sheet after the drying was observed (water resistance test). As a result, no smearing was observed for any types of ink in Examples 1 to 16. It was therefore confirmed that these types of ink had high water resistance.

In addition, the types of ink in examples 1 to 16 were left in an atmosphere of 70°C for three months, and then the state of each ink was observed (stability test). As a result, no coagulation/precipitation was observed in any types of ink.

5 It was therefore confirmed that the types of ink in Examples 1 to 16 had high stability.

Further, for comparison, jetting performance and stability were examined for the following types of ink in Comparative Example 1 (see Japanese Laid-Open Patent
10 Publication No. 10-140055) and Comparative Example 2 (see Japanese Laid-Open Patent Publication No. 2000-154341).

(Comparative Example 1)

C.I. Solvent Black #27 ... 4%

Styrene-acrylic acid copolymer ... 11%

15 Polyetherpolyol water-soluble acrylic resin emulsion

of polyoxyethylene oxypropylene block copolymer

having a number-average degree of polymerization

of oxyethylene of 60 and that of oxypropylene of

45 and glycerin ... 74%

20 Water-soluble acrylic resin emulsion ... 6%

(JOHNCRYL J-61 available from Johnson Polymer Co.)

Triethylene glycol monobutyl ether ... 5%

(Comparative Example 2)

Ink in Comparative Example 2 was prepared in the
25 following manner. First, 2 g of dodecyl sodium sulfate, 4 g of New Frontier S510, 194 g of deionized water, and 10 g of n-butoxymethylacrylamide were put in a flask, and the liquid

was heated to 50°C while stirring under nitrogen gas flow. Thereafter, 5 g of an ethanol solution containing 0.5 g of V-70 (oil-soluble azo polymerization initiator, available from Wako Pure Chemical Industries, Ltd.) was poured in the flask, and subsequently a monomer solution having the following composition was dropped over two hours. The resultant solution was stirred at the same temperature for four hours and then cooled to room temperature, to obtain ink of a colored resin emulsion (Comparative Example 2).

10 Composition of the monomer solution:

n-butoxymethylacrylamide	... 89g
Ethyleneglycol dimethyl methacrylate	... 1g
Savinyl Blue GLS (phthalocyanine blue dye available from Clariant Corp.)	... 6.3g
15 Savinyl Blue RS (anthraquinone blue dye available from Clariant Corp.)	... 18.7g

As for the ink in Comparative Example 1, the viscosity at 25°C was as high as 9800 mPa·s. Using this ink, therefore, printing was not possible with a commercially available ink-jet printer.

As for the ink in Comparative Example 2, the viscosity at 25°C was 5 mPa·s immediately after the preparation of the ink. At this time, printing was possible with a commercially available ink-jet printer. However, when the printer was operated again after being left standing for 24 hours, no jet of the ink was obtained. The ink in Comparative Example 2 was also put in a sealed container and left standing in an

atmosphere of 70°C for three weeks. As a result, the ink was partly coagulated, and the viscosity thereof increased to 1000 mPa·s.

5 In view of the above, unlike the types of ink in Examples 1 to 16, the types of ink in Comparative Examples 1 and 2 described above are found unsuitable for ink-jet recording.

[Effects of the Invention]

10 As described above, the ink for ink-jet recording according to the present invention contains an amphiphilic star polymer of which the outer portion is hydrophilic. Accordingly, oil-soluble dye molecules are captured in the star polymer and thus can be dissolved in water. This suppresses the viscosity of the ink to a low level and
15 improves the stability thereof.

The ink cartridge and the recording apparatus according to the present invention include the ink for ink-jet recording described above, which enables ordinary paper to be performed recording with high printing quality, high image
20 quality, and excellent water resistance.

[Brief Description of the Drawings]

[FIG. 1]

A schematic structural view of an ink-jet recording apparatus in an embodiment of the present invention.

25 [FIG. 2]

A diagrammatic illustration of an amphiphilic star block polymer in the embodiment.

[FIG. 3]

A diagrammatic illustration of an amphiphilic heteroarm star polymer in the embodiment.

[FIG. 4]

5 A diagrammatic illustration of an amphiphilic star block polymer in a comparative example.

[FIG. 5]

A diagrammatic illustration of a star polymer in a comparative example.

10 [FIG. 6]

A diagrammatic illustration of a star polymer in a comparative example.

[FIG. 7]

15 A view illustrating a method for preparing a star polymer.

[FIG. 8]

A view illustrating a method for preparing the amphiphilic star block polymer in the embodiment.

[FIG. 9]

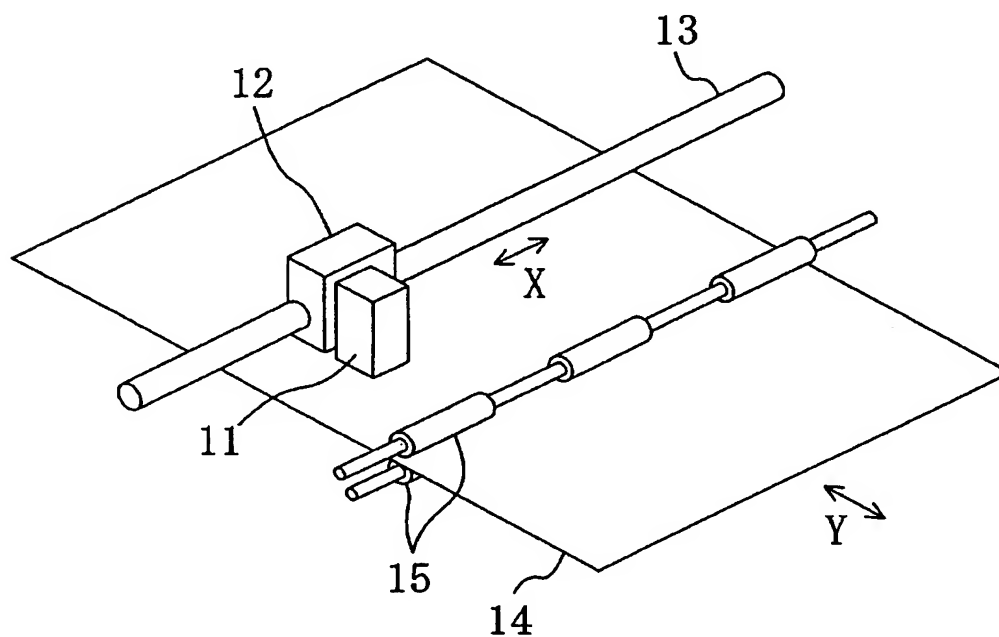
20 A view illustrating a method for preparing the amphiphilic heteroarm star polymer in the embodiment.

[Explanation of the Reference Numerals]

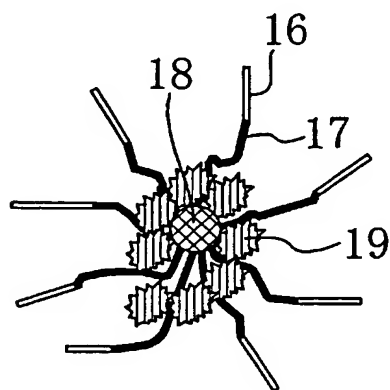
11	ink-jet head
12	carriage
25 13	carriage axis
14	recording paper
15	transport roller

- 16 hydrophilic segment
- 17 hydrophobic segment
- 18 microgel
- 19 oil-soluble dye molecule

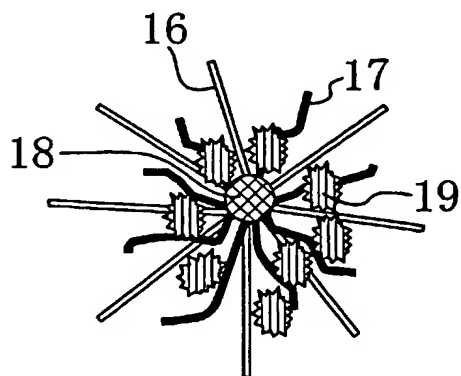
【書類名】 図面
[Name of the Document] DRAWINGS
【図1】
[FIG. 1]



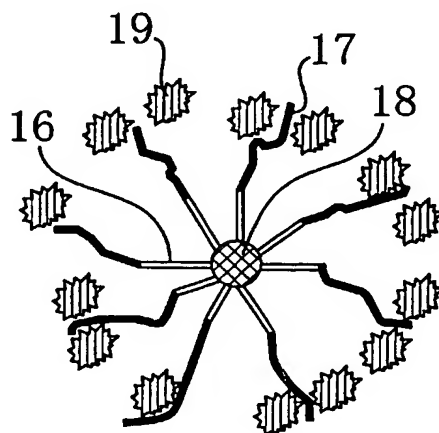
【図2】
[FIG. 2]



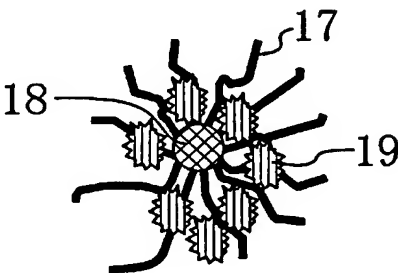
【図3】
[FIG. 3]



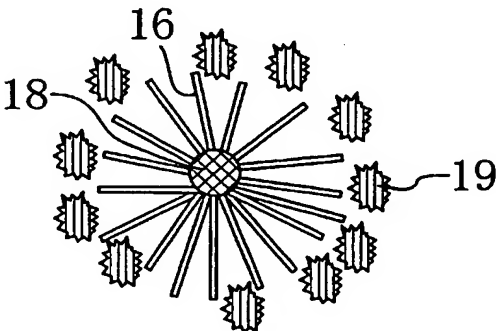
【図4】
[FIG. 4]



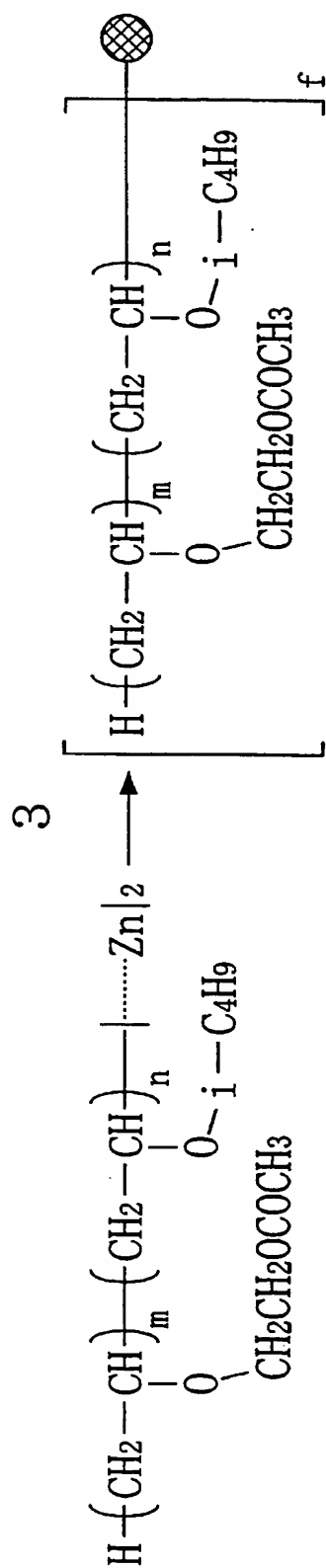
【図5】
[FIG. 5]



【図6】
[FIG. 6]

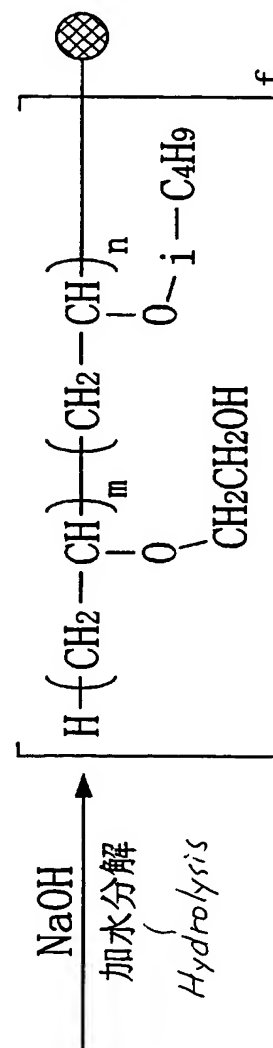


【図8】
[FIG.8]



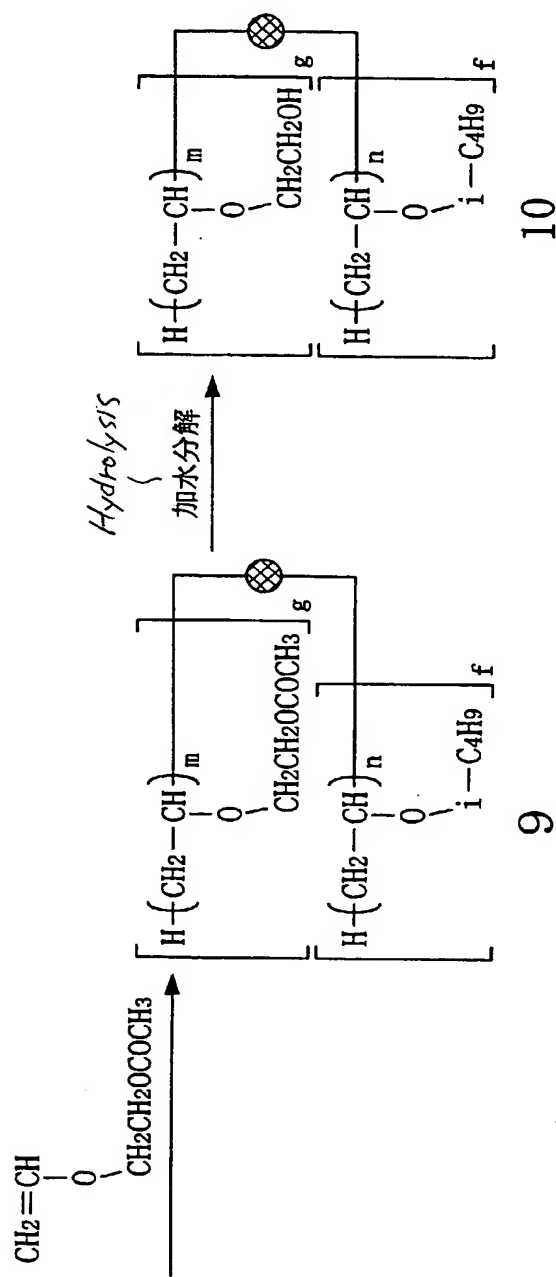
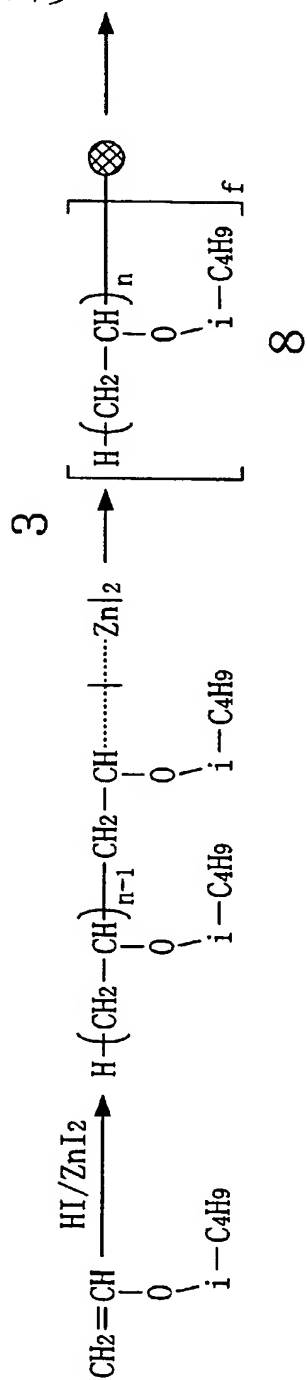
5

6



7

【図9】
[FIG. 9]



[Name of Document] Abstract

[Abstract]

[Purpose] To allow ink for ink-jet recording which contains oil-soluble dye molecules to suppress the viscosity
5 to a low level and improve the stability.

[Solution] The ink of the present invention contains an amphiphilic star block polymer of which the outer portion is hydrophilic. The amphiphilic star block polymer captures oil-soluble dye molecules 19 with its hydrophobic segments 17,
10 while its hydrophilic segments 16 exhibits hydrophilicity. Therefore, it dissolves in water so that oil-soluble dye molecules 19 are kept in its inner portion in high concentration.

[Selected Figure] FIG. 2